



Faculty of Resource Science and Technology

**A COMPARATIVE EVALUATION ON THE OXIDATIVE
APPROACHES FOR EXTRACTION OF HUMIC ACIDS FROM
LOW-GRADE COALS**

Norrafidah Binti Majri

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NORRAFIDAH BINTI MAJRI

This project is submitted in partial fulfilment of the requirements for the degree of
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DECLARATION

No portion of the worked referred to in this dissertation has been submitted in support of an application for another degree of qualification of this any other university or institution of higher learning.

Norrafidah binti Majri

Programme of Resource Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

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A Comparative Evaluation on the Oxidative Approaches for Extraction of Humic Acids from Low-Grade Coals

Norrafidah binti Majri

Resource Chemistry Programme
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

Nowadays, the importance of humic acids as soil fertilizer is fundamental for agriculture community. The oxidation approach with nitric acid was evidenced to increase the yield of humic acids extracted from low-rank coal. However, nitric acid is a very expensive item and therefore not cost-effective especially in producing humic acids at large scale. In this study, hydrogen peroxide (H_2O_2) and alkaline potassium permanganate ($KMnO_4$) were chosen as other oxidizing agents to regenerate the humic acids from low rank coal. The yields, chemical and spectroscopical characteristics of the humic acids extracted were evaluated. The results showed that regenerated coal 10% H_2O_2 produced an average of 86% humic acids, however, the severe loss weight of coal upon oxidation render this approach unfavourable. Oxidation with $KMnO_4$ conversely did not show any improvement in terms of the yield; hence it is not a favourable approach in producing humic acids.

Keywords: humic acids, low-rank coal, oxidation, H_2O_2 , $KMnO_4$

ABSTRAK

Pada masa kini, asid humik yang bertindak sebagai baja tanah amat penting dalam sektor pertanian. Pengoksidaan dengan asid nitrik telah menghasilkan asid humik dalam jumlah yang banyak. Walaubagaimanapun, penggunaan asid nitrik amat mahal dan tidak ekonomi terutamanya dalam penghasilan asid humik dengan kadar yang banyak. Dalam kajian ini, hidrogen peroksida (H_2O_2) dan alkali kalium permanganat ($KMnO_4$) dipilih sebagai agen pengoksidaan untuk menghasilkan asid humik daripada arang batu. Hasil, sifat-sifat kimia dan analisis spektroskopi asid humik telah dikaji. Keputusan menunjukkan bahawa pengoksidaan dengan 10% H_2O_2 telah meningkatkan jumlah asid humik dalam purata 86% tetapi tidak ekonomi disebabkan oleh kehilangan arang batu yang banyak semasa proses pengoksidaan. Sebaliknya, pengoksidaan dengan $KMnO_4$ membuktikan agen ini tidak sesuai bagi penghasilan asid humik kerana tidak menunjukkan peningkatan dalam jumlah asid humik.

Kata kunci: asid humik, arang batu, pengoksidaan, H_2O_2 , $KMnO_4$

1. INTRODUCTION

Humic acids (HAs) occur naturally in aquatic sources, soils, sea sediments, peat, brown-black coals and other chemically and biologically transformed materials (Novák *et al.*, 2001). They are defined as a mixture of natural organic macromolecules with high chemical heterogeneity, which are not soluble in water under acidic conditions with pH below 2 (Li *et al.*, 2004; Ouatmane *et al.*, 2000; Magdaleno and Coichev, 2005). Low-grade coal was found to contain considerable amount of HAs than any other natural resources. A substantial amount of HAs was reported in oxidized lignite or “oxihumolites” in Czech Republic at 70% w/w (Kurková *et al.*, 2004; Carlsen *et al.*, 2000).

Humic substances are known to be an effective natural fertilizer and as soil conditioner. The presence of carboxylic (-COOH) and phenolic (-OH) groups in the HAs have a significant effect on soil structure by improving the soil aggregation. Addition of HAs to loamy and sandy soils was evidence to reduce soil erosion and to recover the physicochemical properties of the soil (Dick *et al.*, 2002; Debska *et al.*, 2002; Kurbanli *et al.*, 2002).

Manufacturers all over the world are promoting the use of HAs product in agriculture and eventually these products are attaining approval by the agriculture community. The common techniques that are employed to prepare cost-effective and large-scale production of humic acid include alkaline extraction, acid precipitation and

membrane separation (Novák *et al.*, 2001). Acid precipitation is the standard method and it is widely used in extracting HAs from solids because of its reliability with claimed value in most products (Fataftah *et al.*, 2001).

In Malaysia, the coal deposit was found at 1,050 million tones of which 69% and 29% are located in Sarawak and Sabah, respectively. To date, the use of the coal resources is focused on the energy production. Non-energy application of the source is largely unexplored. Preliminary study on the application of the Mukah coal resources for agriculture purpose was found to have little potential, as the essential yield obtained was impossible for economic possibilities.

The extraction of HAs with classical acid base fractionation approach only yielded a 20% w/w HAs (Md Nor, 2004). However, pre-treatment of the coal with nitric acids had improved the yield substantially to 80% (Md Nor, 2004). Nitric acid is an effective material but it is an expensive approach, which could add on to the cost of production. Therefore, alternative approaches need to be investigated to evaluate their possibility to be employed for production of humic acids.

2. OBJECTIVES

The aim of this study was to evaluate hydrogen peroxide (H_2O_2) and alkaline potassium permanganate (KMnO_4) oxidations in producing humic acids. The characteristics of the humic acids extracted were also investigated.

3. LITERATURE REVIEW

3.1 Humic Acids

Humic acids (HAs) were positively recommended in the literature to be used as soil amendment to enhance the plant growth. They were reported to have a stimulating effect on soils by increasing the moisture-holding capacity of soil, reducing soil erosion, binding sandy soils, loosening clayey soils, storing and releasing macronutrient and micronutrient elements to plants (Alexander, 1991). They are also important substance for detoxification of hazardous compounds and for control of soil acidity (Wang *et al.*, 2001).

HAs are mainly found in leonardite and lignite. According to prior study, highly oxidized form of lignite such as leonardite has a sufficient amount of HAs and higher oxygen content than lignite (Alexander, 1991). However, the qualities and structures of HAs may differ according to the rank of the coal and the reagents that are employed during oxidation and extraction processes (Garcia *et al.*, 1996). It was revealed that pyrophosphate extraction resulted in HAs with greater oxygen containing functional groups; however KOH extraction produced the greatest yield of humic substances (Garcia *et al.*, 1996).

3.2 Molecular structure and characteristics of humic acids

Numerous efforts were made to research the definite structure of HAs. To date, the exact structure of humic substances remains unknown, as HAs are compounds with high heterogeneity. Despite the complexity, randomness and heterogeneity of HAs, various studies have been performed to evaluate their potential in agriculture and environment. They are found to possess a considerable amount of acidic functional groups (carboxyl groups mainly carboxylic, hydrocarboxylic acids and phenolic groups) that aid for complexation, ion exchange properties and redox active (McCarthy, 2001). The functional characteristics were reported to vary depending the sources, treatment and extraction.

3.3 Oxidative methods

Oxidization on coals causes solubilization of organic matter such as humic acids, thus improving the yield of HAs upon extraction (Alvarez *et al.*, 2003). It has been reported that when coal was oxidized at fixed temperature at 70°C, the development of darkened rims around the outer edges of particles of low rank coal formed, thus these oxidation rims represented as generation of humic acids (Bend and Kosloski, 1993). The HAs generated from the oxidized coal are often referred to as 'regenerated' humic acids. The regeneration of HAs was revealed to depend strongly on the temperature of oxidation (Bend and Kosloski, 1993).

In addition, oxidation methods are very useful for characterizing the humic substances from any sources by trying to simplify the complex structures of humic substances into specific individual monomers (Stevenson, 1985). Cupric oxide (CuO) oxidation has been widely used to characterize ligneous components in humic matter (Hautala *et al.*, 1997). Meanwhile, nitric acid oxidation had introduced oxygen and NO₂ functional groups to HAs (Verheyen *et al.*, 1995).

Several techniques are commonly used for oxidation for example nitric acid (HNO₃), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄) and oxygen. According to Unsal and Ok (2000), these oxidative approaches have improved the yield of humic substances and increased the number of oxygen-containing functional groups such as carboxyl (-COOH) and phenolic-OH groups that have a great influence on the soil fertility.

3.4 Hydrogen peroxide oxidation

Pre-treatment with H₂O₂ on coal has been frequently employed because it is a strong oxidizing agent and the process is inexpensive (Elbeyli and Pişkin, 2004). In addition, this process was found to result in an increase of COOH, OH, C=O, C-O and formation of CO₂ and H₂O gases. The oxidation process was suggested with H₂O₂ at 5% (wt/wt) and a solid/liquid ratio of 1/8 (wt/wt) at 30°C in water bath circulation (Elbeyli and Pişkin, 2004). The FTIR spectra of coal from this treatment demonstrated absorption bands at 2859 cm⁻¹ due to aliphatic hydrocarbon, 2300 cm⁻¹

of C=C groups, 1430 cm^{-1} of CH_2 groups and $1000\text{-}1200\text{ cm}^{-1}$ of C-O alcohols or ether bands.

3.5 Aerial oxidation

Oxidation with oxygen in aqueous alkaline media is referred to as aerial oxidation. In this treatment, the air circulation was performed on lignite at 200°C for 5 hours in the oven. This process was reported to have negative implications especially in transportation and storage (Elbeyli and Pişkin, 2004). According to Juan *et al.* (1990), the alkaline oxidation of coals by air at highest temperature, longest time, lowest alkali concentration and coal-to-alkali ratio were the best conditions to increase the humic acids. Other procedure suggested was by oxidizing the coal at 250°C in air saturated with water vapour for 68 hours (Kurková *et al.*, 2004). Results showed that a higher content of carboxylic acids could be identified in infrared spectra (1710 and 1615 cm^{-1}), aromatic compounds (1615 and 756 cm^{-1}), phenol alcohols (3430 and 1240 cm^{-1}) and a smaller amount of aliphatic hydrocarbons ($2850\text{-}2950\text{ cm}^{-1}$).

3.6 Alkaline permanganate KMnO_4 oxidation

Bajc *et al.* (2001) described the oxidative degradation with alkaline permanganate. This process was performed with 0.5 g KMnO_4 in 10 ml of distilled water in 100 ml of 1% KOH at constant temperature of 70°C . According to Stevenson (1982), the KMnO_4 oxidation process resulted in production of benzene carboxylic acids,

phenolic acids and aliphatic dicarboxylic acids. Bone *et al.* (1926-37) reported that this process produced a significant amount of crystalline benzenoid acids, oxalic acid and acetic acid. These acids were derived from the formation of intermediate colloidal "humic" acids (Van Krevelen, 1993). Other study reported that when the permanganate oxidation was carried out at 90°C, the major products were benzenepolycarboxylic acids, phenolic acids and fatty acids. While, alkanolic acids were the dominant compounds appeared after the similar oxidation process performed at room temperature (Almendros and Martín, 1989).

3.7 Peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$) and peroxyacetic acid ($\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$) oxidations

The peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$) oxidation produced as similar compounds as alkaline KMnO_4 and Cu-NaOH oxidations. Major products of phenolic acids (4.3%) and benzene carboxylic acids (15.2%) were identified in HAs from this oxidation process (Stevenson, 1982). Other oxidizing agent was peroxyacetic acid ($\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$). This treatment produced major substances of benzene carboxylic acids (36%), toluene carboxylic acids (75%), furan- and methyl furan-carboxylic acids (16%) and dibasic aliphatic acids (18%) (Van Krevelen, 1993).

3.8 Alkaline cupric oxide (Cu-NaOH) oxidation

This is a mild oxidation process that is used extensively in lignin chemistry. This treatment was performed with 5*N* NaOH at 170°C and 250°C with CuSO₄ addition (Stevenson, 1982). The products produced in humic substances were primarily a variety of phenolic compounds at 6% of total organic matter for reaction at 250°C and 2% at 170°C and benzene carboxylic acids (15%). Other products were fatty acid methyl esters, alkanes, aliphatic dicarboxylic acid esters and dioctyl adipate.

4. MATERIALS AND METHODS

4.1 Coal samples

Coal samples from Mukah, Sarawak were used for this study. The coal samples were pulverised and sieved through 50 μ m sieve prior oxidation and extraction.

4.2 Oxidative pre-treatment

4.2.1 *Hydrogen Peroxide (H₂O₂)*

The oxidizing procedure was based on procedure described by Elbeyli and Pişkin (2004). One gram of coal sample was treated with 8 g of H₂O₂ solution at 5% in water bath circulation at constant temperature of 70°C. The mixture was stirred for 2 hours and sieved through 50 μ m sieve to obtain oxidized coal. The treated coal was dried in oven at 105°C for overnight. The oxidized coal was weighed before and after oxidation. The procedure was repeated with 10% H₂O₂ with the above procedure.

4.2.2 *Alkaline Permanganate (KMnO₄)*

One gram of coal was oxidized with 5% and 10% of potassium permanganate in alkaline solution. The mixture was stirred for 2 hours at constant temperature of 70°C

and filtered through 50 μ m sieve to obtain oxidized coal. The treated coal was dried at 105°C overnight. The oxidized coal was weighed before and after oxidation.

4.3 Extraction of humic acids

The humic acids (HAs) were isolated from coal samples according to standard procedure described by Swift (1996) with slight modifications. One gram of coal samples was treated with 10 ml of 0.5M KOH at 70°C for 2 hours. The supernatant was filtered through 50 μ m sieve and the coal residue was washed with distilled water until the supernatant was clear. The coal residue was dried at 105°C overnight and weighed. The HAs were separated from fulvic acids by precipitation with concentrated H₂SO₄ to pH 1-2. The precipitated HAs were centrifuged at 6000 rpm for 15 minutes. The HAs were washed with distilled water, centrifuged again and dried at 60°C in oven. The HAs samples were weighed and kept in desiccators for further analyses.

4.4 Yield of humic acids

The yield of HAs was calculated as the weight of extracted humic acids per unit weight of coal.

4.5 Characterization of humic acids

4.5.1 *Moisture content*

Moisture contents of the extracted humic acids were calculated from differences in weights before and after drying in oven at 105°C for overnight (Md Nor, 2004)

4.5.2 *Ash content*

The ash content of the extracted humic acids was obtained after ignition in furnace at 800°C for 2 hours (Md Nor, 2004).

4.5.3 *Total acidity (COOH and phenolic-OH)*

Approximately 50 to 100 mg of HAs sample were dissolved in 20 ml of 0.2N Ba(OH)₂ solution. The air in the sample was displaced with N₂ and shaken for 24 hours. The suspension was filtered and the filtrate was titrated with 0.5M HCl to pH 8.4. A blank consisting of 20 ml of 0.2N Ba(OH)₂ was prepared simultaneously (Md Nor, 2004).

Total acidity (in meq/g) was calculated with the equation below:

$$\text{Total acidity} = \frac{(V_b - V_s) \times N}{\text{g of sample}}$$

Where,

V_b = volume of standard acid for blank

V_s = volume of standard acid for sample

N = concentration of HCl

4.5.4 Carboxyl groups (-COOH)

Approximately 50 to 100 mg of HAs sample were dissolved in 10 ml of 0.5M $\text{Ca}(\text{CH}_3\text{COO})_2$ solution and 40 ml of distilled water and were shaken for 24 hours. The suspension was filtered and the filtrate was titrated with 0.1M NaOH to pH 9.8. A blank consisting of 10 ml of 0.5M $\text{Ca}(\text{CH}_3\text{COO})_2$ was prepared simultaneously (Md Nor, 2004).

The content of COOH groups (meq/g) were calculated with this equation:

$$\text{COOH groups} = \frac{(V_s - V_b) \times N}{\text{g of sample}}$$

Where,

V_b = volume of standard base for blank

V_s = volume of standard base for sample

N = concentration of NaOH

4.5.5 Phenolic group (-OH)

The quantity of phenolic OH content was calculated as the different between the total acidity (meq/g) and the COOH content (meq/g) (Md Nor, 2004).

$$\text{Phenolic OH} = \text{total acidity} - \text{COOH}$$

4.6 Spectroscopic analyses

4.6.1 Infrared spectroscopy (FTIR)

The infrared spectra were recorded on a *Perkin Elmer* spectrophotometer at a resolution of 4cm^{-1} in the range of $400\text{-}4000\text{cm}^{-1}$. Pellets were obtained by weighing 1 mg of dried humic acids sample and 100 mg KBr. Deconvolution method was carried out according to Yürüm and Altuntaş (1998). The total peak area was calculated by measuring the amount of total peak area for each of the deconvoluted peaks in the range of $1780\text{-}1500\text{ cm}^{-1}$.

4.6.2 UV-Vis spectroscopy

The E_4/E_6 ratios were determined by dissolving 5.0 mg of humic acids in 25 mL of 0.05 M NaHCO_3 solution (pH range between 9.1-9.5). The absorbance at 465 nm and 665 nm were recorded on a *Perkin Elmer Lambda 11 UV-VIS* spectrophotometer.